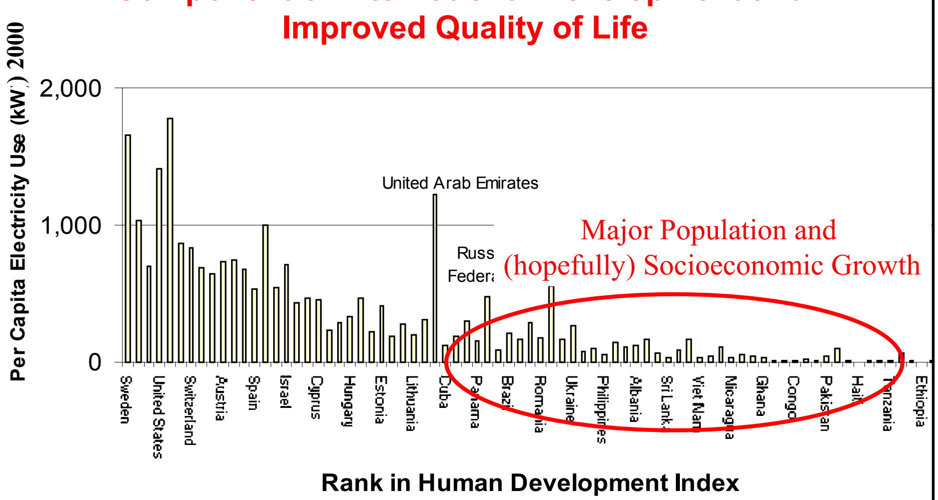
Catalysis in the Atom and Energy Economy

May 25th, 2004 2:00-3:40pm

Catalysis will continue to play a major and critical role in producing the chemicals and fuels essential for the U.S. prosperity far into the future.

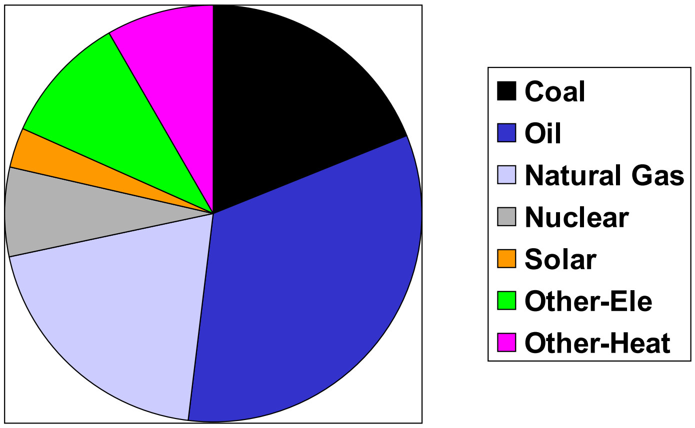
- What key advances are needed to tackle the challenges in our atom-economy and energy-economy?
- Is the DOE overlooking support in areas of catalysis with the potential for significant impact?
  - New chemistry and catalysts to efficiently convert the old sources (fossil, renewable, solar)?
  - New energy carriers (H2 and beyond, electrocatalysis)?
  - Catalytic processing under extreme environments: very high temperature, very low temperature, plasmas, electric fields?

The Availability of Low Cost Energy is an Essential Component of International Development and Improved Quality of Life

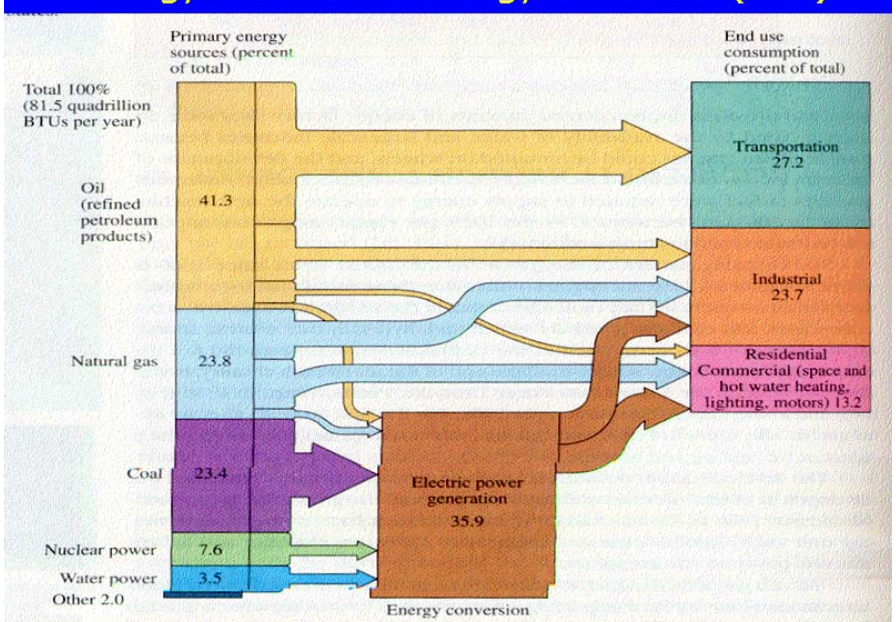


From UN Human Development Report 2003 commissioned by the United Nations Development Programme (UNDP).
http://www.undp.org/hdr2003/indicator/indic_176_1_1.html

US Energy Consumption 2003: 99 quadrillion Btu

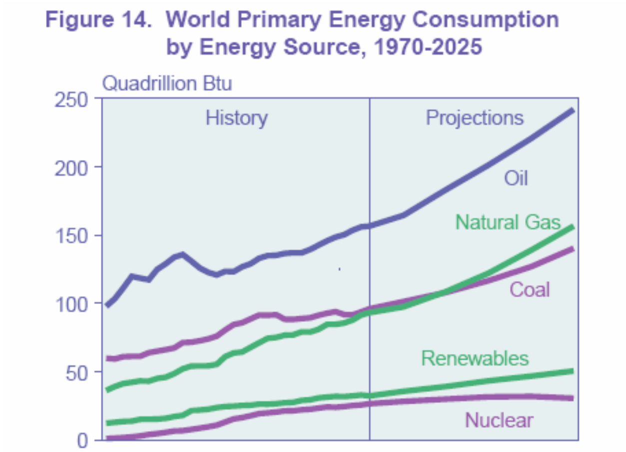


Energy sources vs. energy utilization (USA)



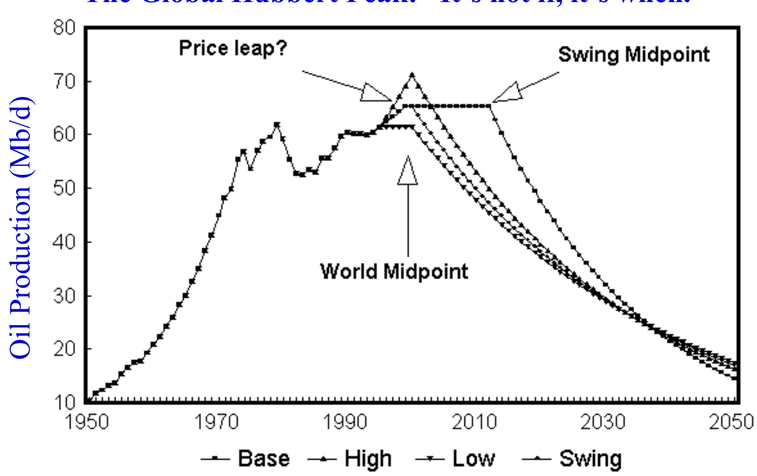
http://teaching.ust.hk/~chem342/leture_notes/2

WORLD USE: EIA Predictions



Sources: **History:** Energy Information Administration (EIA), *International Energy Annual 2001*, DOE/EIA-0219(2001) (Washington, DC, February 2003), web site www.eia.doe.gov/iea/. **Projections:** EIA, System for the Analysis of Global Energy Markets (2004).

The Global Hubbert Peak: It's not if, it's when.

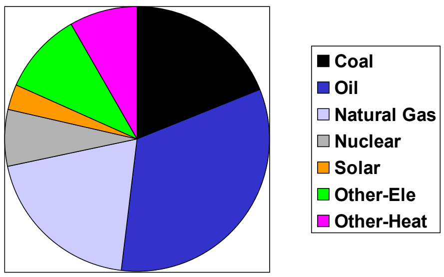


This graph (often referred to as the "Hubbert Curve,") is based on an Ultimate Recovery of conventional oil of 1750 Gb (Giga = Billion barrels), and depicts alternative scenarios of production. The Swing Case assumes a price leap when the share of world production from a few Middle East countries reaches 30%. This is expected to curb demand, leading to a plateau of output until the Swing countries reach the midpoint of their depletion, when resource constraints force down output at the then depletion rate. [from The Twenty First Century, The World's Endowment of Conventional Oil and its Depletion, by Dr. Colin Campbell, 1996]

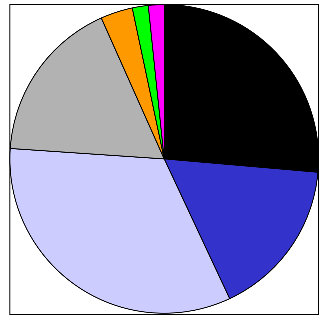
http://www.hubbertpeak.com/images/cam18.gif

US Energy Consumption

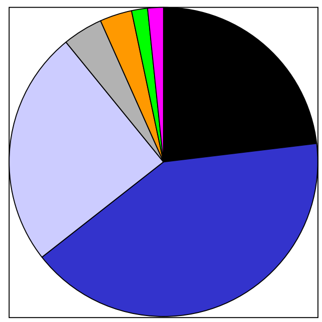
2003: 99 quadrillion Btu



EWM Projection

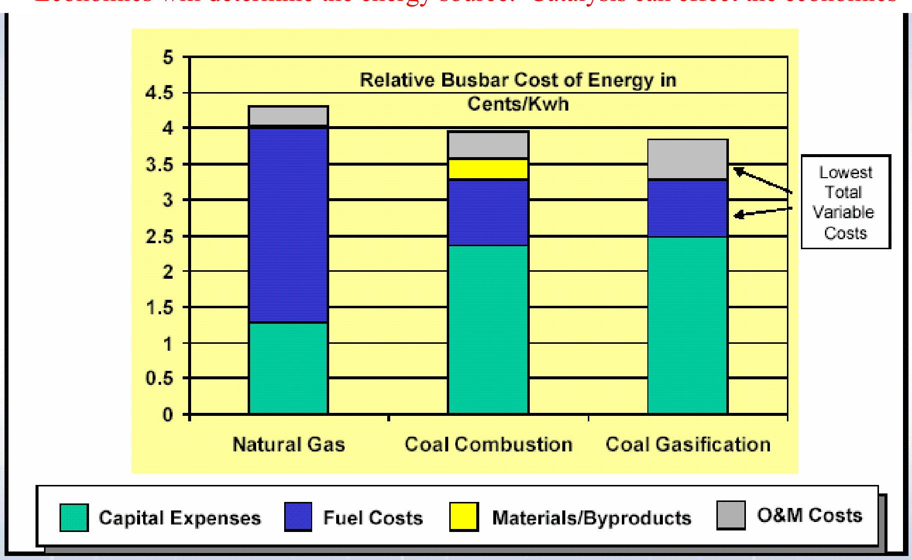


2025: 137 quadrillion Btu



EIA Projection

Economics will determine the energy source: Catalysis can effect the economics

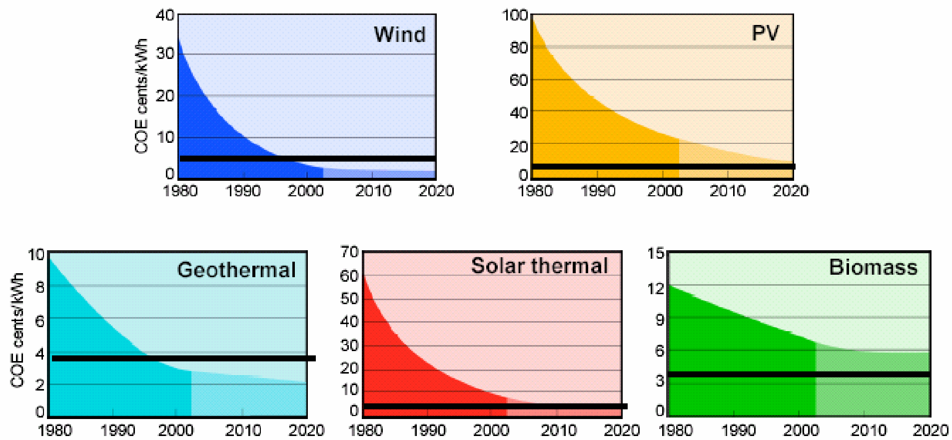


Assumptions: Nat. Gas - 65% capacity factor w/ fuel costs of $4/MM Btu and capital costs of $500/kW;
Coal Combustion - SCPC plant at 85% capacity factor w/ fuel costs of $1.25/MM Btu and capital costs of $1,200/kW;
Coal Gas - IGCC plant at 85% capacity factor w/fuel costs of $1.25/MM Btu and capital costs of $1,250/KW.

EASTMAN Data extrapolated from DOE Report "Market-Based Advanced Coal Power Systems", May 1999.

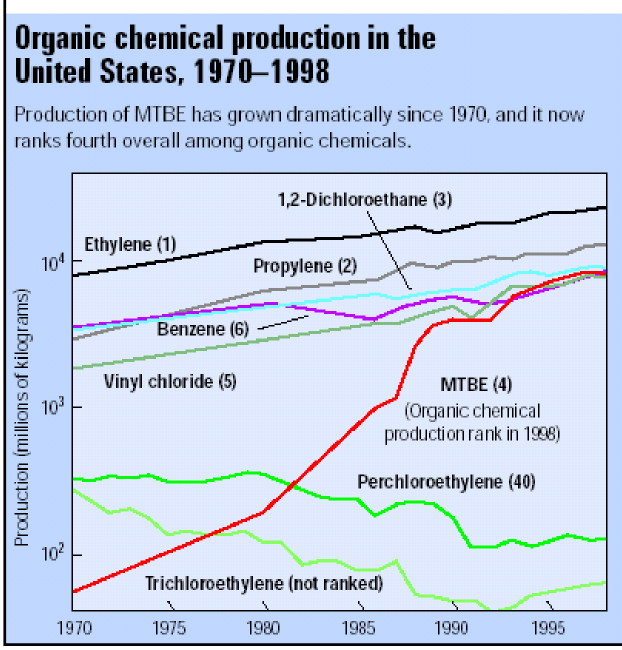
The Cost of Renewable Energy

Levelized cents/kWh in constant $2000



Source: NREL Energy Analysis Office
These graphs are reflections of historical cost trends NOT precise annual historical data.
Updated: October 2002

Future Sources of Chemical Feedstocks



Major Feedstock(s)
Exxon-Mobil (Oil,NG ->NG)
Shell (Oil,NG -> NG)
Dupont (Oil,NG->Biomass,NG)
Dow(NG,Oil ->NG, Biomass)
Sasol (Coal ->NG, Coal)
BP (Oil,NG -> NG)

"Mature" Technologies

The single most energy consuming step in the petrochemical industry is the thermal cracking of hydrocarbon feedstocks. "At $41/barrel we'll crack $4.5 MBTU gas all day long"

Table 6. 1994 Estimated U.S. final energy consumption (HHV) for selected key chemicals. (including feedstocks)

Product	Estimated Final Energy SEC (GJ/tonne)	1994 Production (million tonnes)	Estimated Total Energy Use in 1994 (PJ)	Percent Share of SIC 28 Energy Use (%)
Ethylene and co-products	67.5	26.2	1768	29.3%
Methanol	38.4	4.9	188	3.1%
Polyethylene	9.3	5.7	53	0.9%
Polypropylene	10.5	4.4	45	0.7%
Polyvinyl Chloride	11.6	5.4	62	1.0%
Polystyrene	9.3	2.6	24	0.4%
Nitrogen	1.8	28.6	49	0.8%
Oxygen	1.8	22.7	44	0.7%
Ammonia	39.8	16.2	645	10.5%
Urea	2.8	7.6	21	0.3%
Chlorine	19.2	11.1	213	3.5%
Total			**3112**	**51.5%**

[1]Co-products include propylene, benzene, and butadiene. SEC reflects energy per ton of all high value products from steam cracking.
[2]The SEC, or Specific Energy Consumption estimates are preliminary. Sources for SEC are as follows: ethylene and co-products (see Chapter 3), methanol and urea (Lipinksy and Ingham, 1994), polyethylene, polypropylene, polyvinyl chloride (Lipinsky and Wesson, 1995), Nitrogen and Oxygen (OTA, 1993), ammonia (see Chapter 4), chlorine (see Chapter 5). Production estimates are from CMA (1996).

ALSO: Separation energy costs (ethane/ethylene) are considerable

AND: Large quantities of carbon dioxide are produced

Atom and Energy Economy

May 25th, 2004 2:00-3:40pm

Starting Points for Discussion

1) Catalysis will continue to play a major and critical role in producing the chemicals and fuels essential for the U.S. prosperity far into the future.
   - How can we educate enough qualified people? Are there sufficient resources for "human resources"?
2) Hydrocarbons from fossil and biomass sources will continue to dominate the fuels and chemicals landscape far into the future.
   - Improved C-C, C-H utilization
   - Biomass to chemicals (not fuels ?)
   - CO2 reduction chemistry
3) Electricity and heat from nuclear, wind, solar, and other non-combustion sources will become increasingly available.
   - Electrocatalysis
   - CO2 reduction electrochemistry, electrosynthesis
   - Opportunities for catalytic processing in extreme environments: very high temperature, very low temperature, plasmas, electric fields?
4) There will always be a variety of different feedstocks and fuels. Economic considerations will determine which new energy systems and processes are adopted on large scales.
   - Carbon economy? / Hydrocarbon economy? => Hydrocarbon economy
   - Electron Economy.

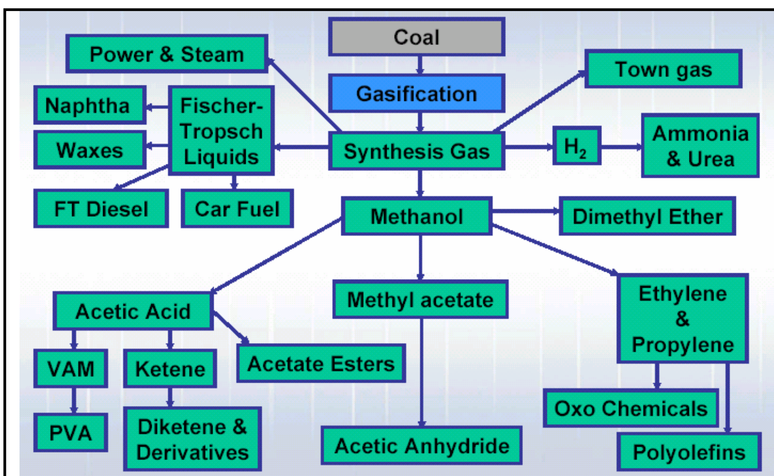
Atom and Energy Economy

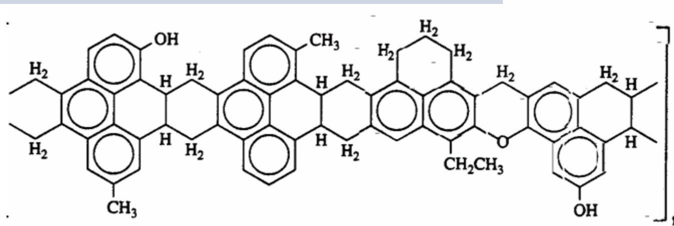
May 25th, 2004 2:00-3:40pm

1) Catalysis will continue to play a major and critical role in producing the chemicals and fuels essential for the U.S. prosperity far into the future.
   - **How can we educate enough qualified people? Are there sufficient resources for "human resources"?**

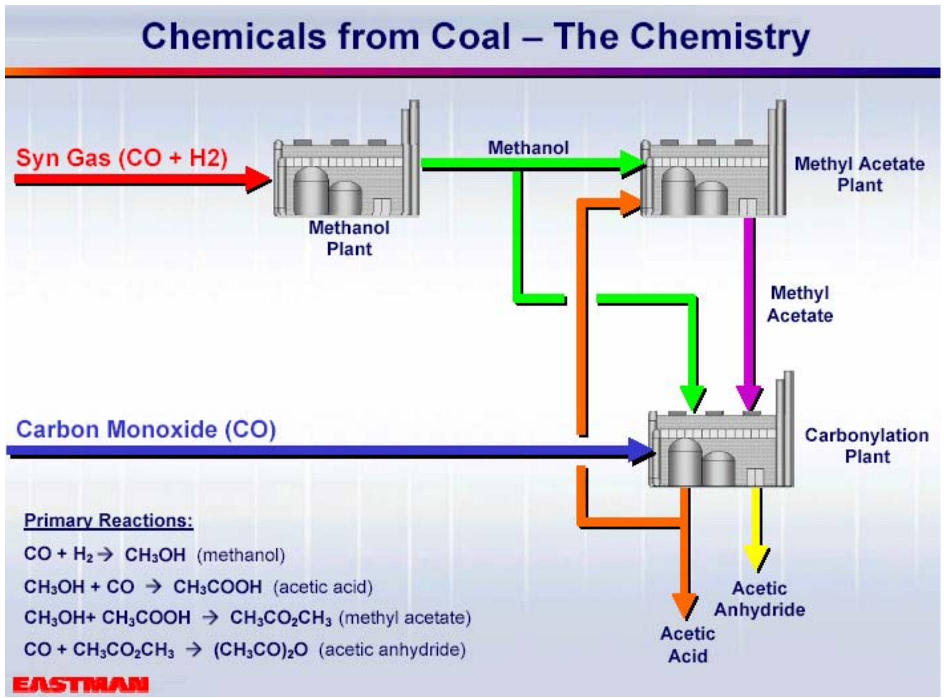
The Most Important Resource in Any Organization is the Human Resource.

- What can we do?
  - Use the present "excitement" about energy and the environment to attract the best young people into catalysis.
- What do we want to tell DOE BES?
  - We need adequate graduate student and post doc training funds. The day of the \$30k post doc is gone (or should be) average ~ \$50k.
  - Provide separate "Education Funds" for each project where the output is educational experiences.
  - Recruiting is not free, it takes time and money. Allow recruiting funds on proposals.
  - Help us bring in foreign students and post-docs!





Representative structure of bituminous coal



Coal

		Major Challenges in Catalysis	Basic Science Challenges	Where DOE is missing something
Coal	Production			
Coal	Utilization	Gassification, Combustion, FT, CO Syngas Synthesis	Syngas synthesis, reactive separation, CO utilization	
Coal	Clean-Up	CO2, NOx reduction, S, Particulates	CO2 NOx reduction chemistry	

	(0,1,2,3)	Impact on US Economy In 2025	Likelihood Catalysis can Have a Major Impact by 2025	Impact on the Environment Of success in catalysis	Total	Magnitude of minimum effort required for success over 25 years	
Coal	Production Utilization (gasification) Clean-Up (CO2, S,Part)	3 3 3	0 2 3	0 2 3	3 7 9		

S. Overbury

- catalysts based on inexpensive metals (replace precious metals)
  - TM carbides for anodes in fuel cells
    - known activity for H_2 activation
    - metallic conductors
    - resistant to CO adsorption
    - but surface unstable in air
    - possibly high S tolerance
- New catalysts for fuel cells
  - Carbon catalysts active for selective S oxidation (H_2S to S) but… possibly important role of impurities
  - useful for fuel reforming in front of fuel cells
- Novel ways to improve hetero catalyst longevity and selectivity
    - uranium oxide catalysts
      - resistant to Cl poisoning
      - active for catalytic combustion of chlorinated VOCs
      - competitive with Pt for combustion, but cheaper
    - cerium oxide supported metals
      - selective oxidation catalysts
      - reducible support alters properties of precious metal

Natural Gas

		Major Challenges in Catalysis	Basic Science Challenges	Where DOE is missing something
NG	Production			
NG	Utilization	FT, other GTL, H2 production	C-H bond activation	
NG	Clean-up	CO2 reduction ->HC's NOx reduction	CO2 NOx reduction chemistry	

	(0,1,2,3)	Impact on US Economy In 2025	Likelihood Catalysis can Have a Major Impact by 2025	Impact on the Environment Of success in catalysis		Magnitude of minimum effort required for success over 25 years	
NG	Production	3	0	0	3		
	Utilization (GTL, H2)	3	2	2	7		
	Clean-up (CO2)	3	3	3	9		

Oil

		Major Challenges in Catalysis	Basic Science Challenges	Where DOE is missing something
Oil	Production			
Oil	Utilization	Catalytic combustion		
Oil	Clean-up	CO_2 reduction ->HC's	CO_2 NO_x reduction chemistry	

	(0,1,2,3)	Impact on US Economy In 2025	Likelihood Catalysis can Have a Major Impact by 2025	Impact on the Environment Of success in catalysis		Magnitude of minimum effort required for success over 25 years	
Oil	Production Utilization Clean-up (CO_2)	3 3 3	0 2 3	0 2 3	3 7 9		

Nuclear

		Major Challenges in Catalysis	Basic Science Challenges	Where DOE is missing something
Nuclear	Production			
Nuclear	Utilization	Electrocatalysis (H_2, hydrocarbs)	CO_2 reduction chemistry	
Nuclear	Clean-up	Electrosynthesis		

	(0,1,2,3)	Impact on US Economy In 2025	Likelihood Catalysis can Have a Major Impact by 2025	Impact on the Environment Of success in catalysis		Magnitude of minimum effort required for success over 25 years	
Nuc	Production Utilization (electrocat) Clean-up (Rad, Cor,)	2 2 3	0 3 1?	0 3 3	2 7 7		

Biomass

		Major Challenges in Catalysis	Basic Science Challenges	Where DOE is missing something
Biomass	Production			
Biomass	Utilization			
Biomass	Clean-up			

•(A. Bell) Biomass for chemicals and fuels – Is it practical? How can catalysis be used to convert bio-derived feedstocks to chemicals and fuel components?

	(0,1,2,3)	Impact on US Economy In 2025	Likelihood Catalysis can Have a Major Impact by 2025	Impact on the Environment Of success in catalysis		Magnitude of minimum effort required for success over 25 years	
Biomass	Production Utilization (ethanol,H2) Clean-up (CO2, C)	2 1 1	1 3 3	3 2 1	6 6 5		

J. Dumesic

Production of Energy and Chemicals from Renewable Biomass Resources

Catalytic context:

The past 50 years of catalysis research have addressed how to ***add*** functionality to non-renewable fossil fuel resources (*e.g.*, partial oxidation)

Biomass-derived compounds, such as carbohydrates, have ***excess*** functionality (*e.g.*, glucose = $C_6O_6H_{12}$)

J. Dumesic

Catalytic challenge:

To identify new catalytic processes that allow the effective utilization of renewable biomass-derived compounds by:

taking advantage of the high inherent functionality of these compounds

selectively removing the excess functionality of these compounds

Basic science challenges for catalytic utilization of renewable biomass-derived compounds:

Taking advantage of the high inherent functionality of these compounds

- Selective oxidation of specific -C-OH to –C=O
- Selective polymerization reactions

Selectively removing the excess functionality of these compounds

- Selective dehydration
- Selective hydrogenation of specific C=C, C=O groups

Developing new materials that are stable under the high T, aqueous conditions needed to process these compounds

- catalyst supports and active phases that do not sinter and are not leached into the aqueous environment

J. Dumesic

S. Overbury

- Other chemical energy carriers besides H_2
  - Gasoline is perfect fuel !
    - If use electricity to produce H_2 from H_2O (“hydrogen economy”) why not use electricity to produce $–(CH_2)–$ from CO_2 and H_2O ?
      - » H_2O to H_2 (electrolytic or photolytic)
      - » (sequestered) CO_2 to CO by WGS
      - » CO $+H_2$ to $–(CH_2)–$ by FT
    - carbon neutral (ignoring electricity production)

- Challenges and opportunities in carrying out reactions at very low temperature
  - Au active for oxidation at room temperature
    - room temperature deodorants
    - passive pollution control (wall mounted domestic CO removal)

Solar

		Major Challenges in Catalysis	Basic Science Challenges	Where DOE is missing something
Solar	Production			
Solar	Utilization	Photocatalysis, Electrocatalysis	Electron transfer reactions	
Solar	Clean-up	Detox, Water purification		

•(A. Bell)How can catalysis contribute to the photo-electrochemical generation of H2?

	(0,1,2,3)	Impact on US Economy In 2025	Likelihood Catalysis can Have a Major Impact by 2025	Impact on the Environment Of success in catalysis		Magnitude of minimum effort required for success over 25 years	
Solar	Production (PV,photocat) Utilization (electrocat) Clean-up	1 1 1	1 2 1	3 3 3	5 6 5		

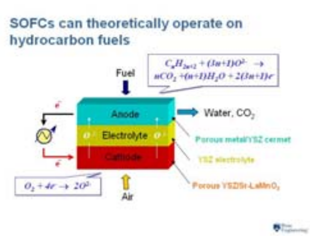
Hydrogen ? Fuel Cells?

- (A.Bell) Can one find a substitute for Pt in fuel cells? What are the scientific challenges?

Surface Chemistry and Catalysis have much to offer in Solid-State Electrochemistry.

R. Gorte

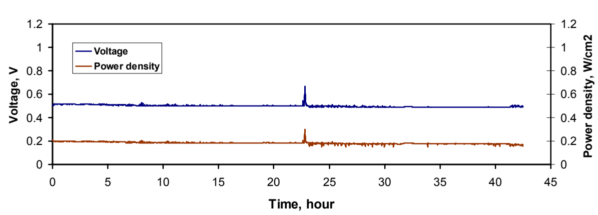
Direct-Oxidation SOFC-



Upon heating in toluene at 700°C.

Cu Ni

15%CeO2 25%Cu, 24um electrolyte, laminated cell, LSF, Heavy Naph 700 oC



Clever ideas for H_2 production using electrochemistry:

R. Gorte

Membrane reactors (Air Products, Ceramatec, etc.)

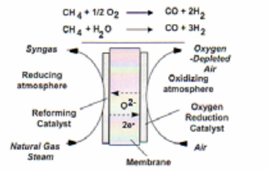
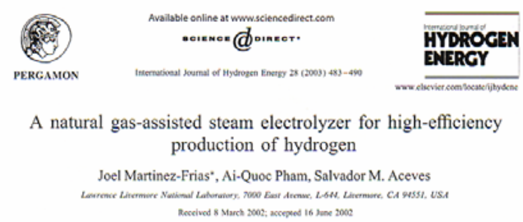


Figure 1. The conceptual ITM Syngas technology.

Novel Electrolysis Concepts (LLNL)

"…system efficiency is up to 70% with respect to primary energy."



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International Journal of Hydrogen Energy 28 (2003) 483–490

International Journal of HYDROGEN ENERGY

www.elsevier.com/locate/ijhydene

A natural gas-assisted steam electrolyzer for high-efficiency production of hydrogen

Joel Martinez-Frias*, Ai-Quoc Pham, Salvador M. Aceves

Lawrence Livermore National Laboratory, 7000 East Avenue, L-644, Livermore, CA 94551, USA

Received 8 March 2002; accepted 16 June 2002

"Alloy" Catalysts for H_2 Production:

R. Gorte

Pd-ZnO Methanol Reforming (PNNL)

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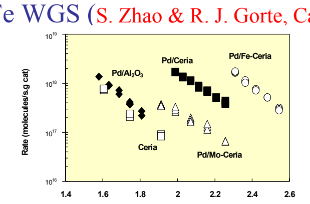
APPLIED CATALYSIS A: GENERAL

Kinetic studies of methanol steam reforming over Pd/ZnO catalyst using a microchannel reactor

Chunshe Cao*, Gordon Xia, Jamie Holladay, Evan Jones, Yong Wang

Pd-Fe WGS (S. Zhao & R. J. Gorte, Catal. Lett., 92 (2004) 75)



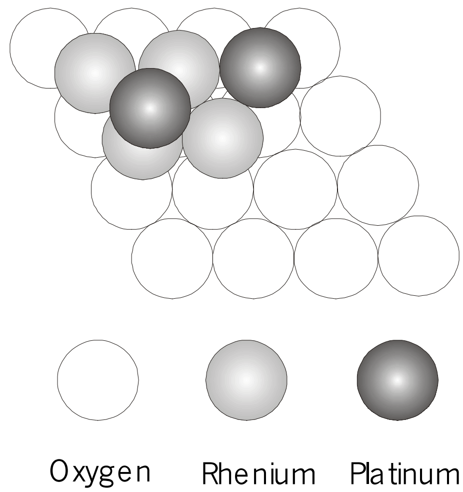
Cu-Co Reforming Catalysts? **(samples heated in CH_4 for 3 h at 800ºC)**

100% Cu　　100%Co

90%Co-10%Cu

Re_4Pt_2 formed from $Re_2Pt(CO)_{12}$ supported on Al_2O_3 : CATIONIC PLATFORM FOR NOBLE METAL CLUSTER

Bruce Gates



Fung, Kelley, Koningsberger, Gates, *J. Am. Chem. Soc.*, 119, 5877 (1997).

BIMETALLIC PRECURSORS WITH OXOPHILIC AND NOBLE METALS

$Pt[W(CO)_3(C_5H_5)]_2(PhCN)_2$
$Pt_2W_2(CO)_6(C_5H_5)_2(PPh_3)_2$
$Pd_2Mo_2(C_5H_5)_2(CO)_6(PPh_3)_2$
$PtW_2(CO)_6(C_5H_5)_2(PhCN)_2$
$PtMo_2(CO)_6(C_5H_5)_2(PhCN)_2$

Bruce Gates

OXOPHILIC METALS PROVIDE SITE-ISOLATED NANO-SUPPORTS FOR NOBLE METALS

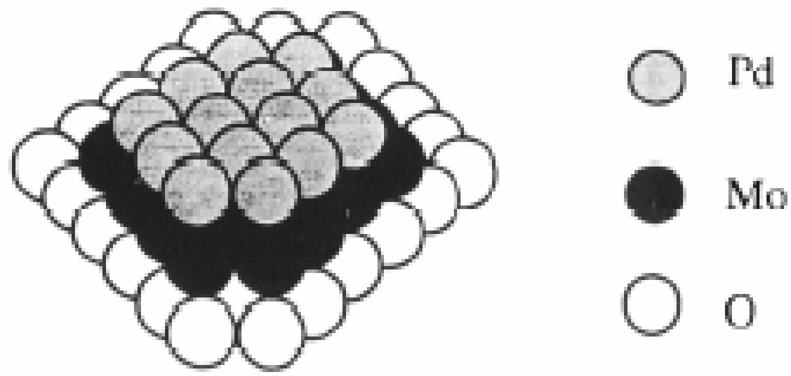


Figure 9. Simplified structural model of a bilayer consisting of molybdenum cations interacting with the MgO support and providing a platform for the highly dispersed palladium. According to this model, the molybdenum helps to maintain the dispersion of the palladium.

Kawi, Alexeev, Shelef, Gates, *J. Phys. Chem.* **99**, 6926 (1995).

Bruce Gates

STABILIZATION OF NOBLE METALS BY DISPERSION ON NANOSUPPORTS

- **OXOPHILIC METAL CATIONS BONDED TO SUPPORT PROVIDE NEST FOR DISPERSION OF NOBLE METAL**

- **SOME COMBINATIONS STABLE IN O_2 & in H_2 AT TEMPERATURES UP TO 400 ºC**

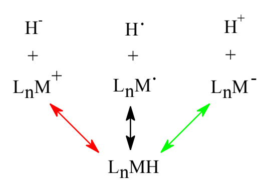
- **MAY PROVIDE METHOD WITH SOME GENERALITY FOR STABILIZATION OF NOBLE METALS IN HIGH DISPERSIONS**

Understanding the Energetics of Transition Metal Hydrides:
Its Central Role in Hydrogen Storage,
Hydrogen Separation and Purification,
Catalyst Design,
and Bio-Inspired Hydrogen Production/Utilization

Dan DuBois

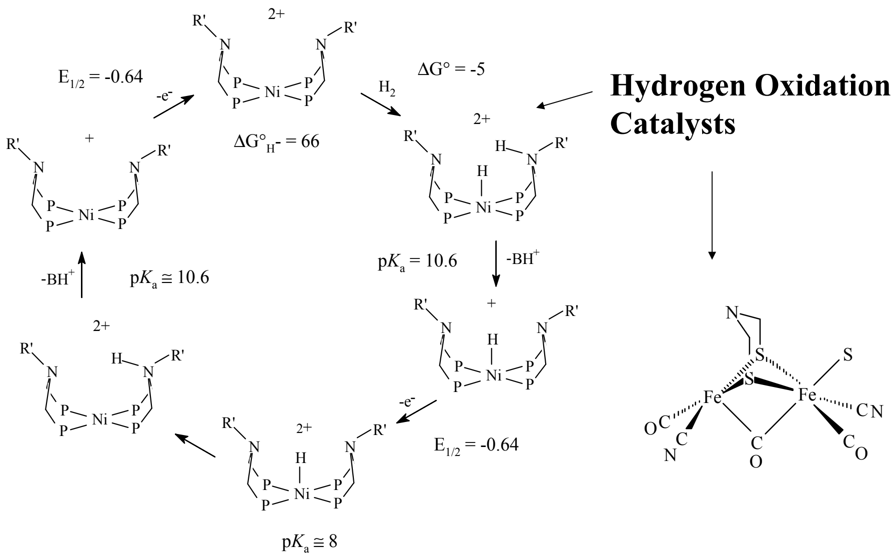
National Renewable Energy Laboratory

Types of M-H Bond Cleavage Reactions



Understanding the energetics of these three bond dissociation reactions provides the basis for a wide range of applications including hydrogen storage, catalyst design, hydrogen separation, and an understanding of the features affecting the energetics of hydrogenase enzymes.

At molecular scale energetics must be correct and physical pathways for proton-, hydride-, and electron-transfer must exist.

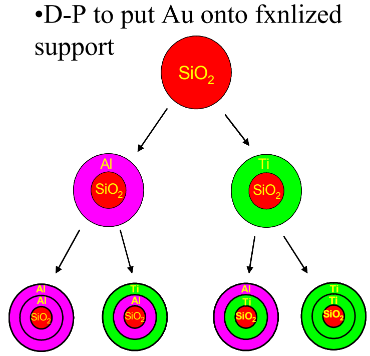


S. Overbury

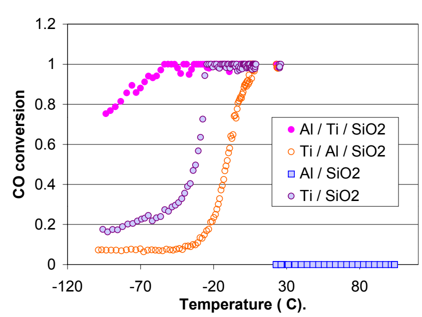
Novel ways to improve catalyst selectivity

Tailored layer-by-layer supports

- sequential layer growth on amorphous nanoparticles of non-porous SiO_2 (Cabo-Sil)
- can use Ti, Zr, Al, Ge…
- D-P to put Au onto fxnlized support



activity for CO oxidation depends critically on surface of support



What else are we missing?

		Major Challenges in Catalysis	Basic Science Challenges	Where DOE is missing something
Other	Production			
Other	Utilization	electrosynthesis		
Other	Clean-up			

	(0,1,2,3)	Impact on US Economy In 2025	Likelihood Catalysis can Have a Major Impact by 2025	Impact on the Environment Of success in catalysis		Magnitude of minimum effort required for success over 25 years	
Other	Production Utilization (electrocat) Clean-up						